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(54) Crystalline anhydrous maltitol

(57) Crystalline anhydrous maltitol  
having a melting point of 146.5—  
147.0°C is prepared by (a)  
crystallising a solution containing

maltitol and harvesting the resultant  
crystals of anhydrous maltitol from the  
solution or

(b) crystallising a solution  
containing maltitol and solidifying the  
resultant manecuite into a crystalline  
solid.

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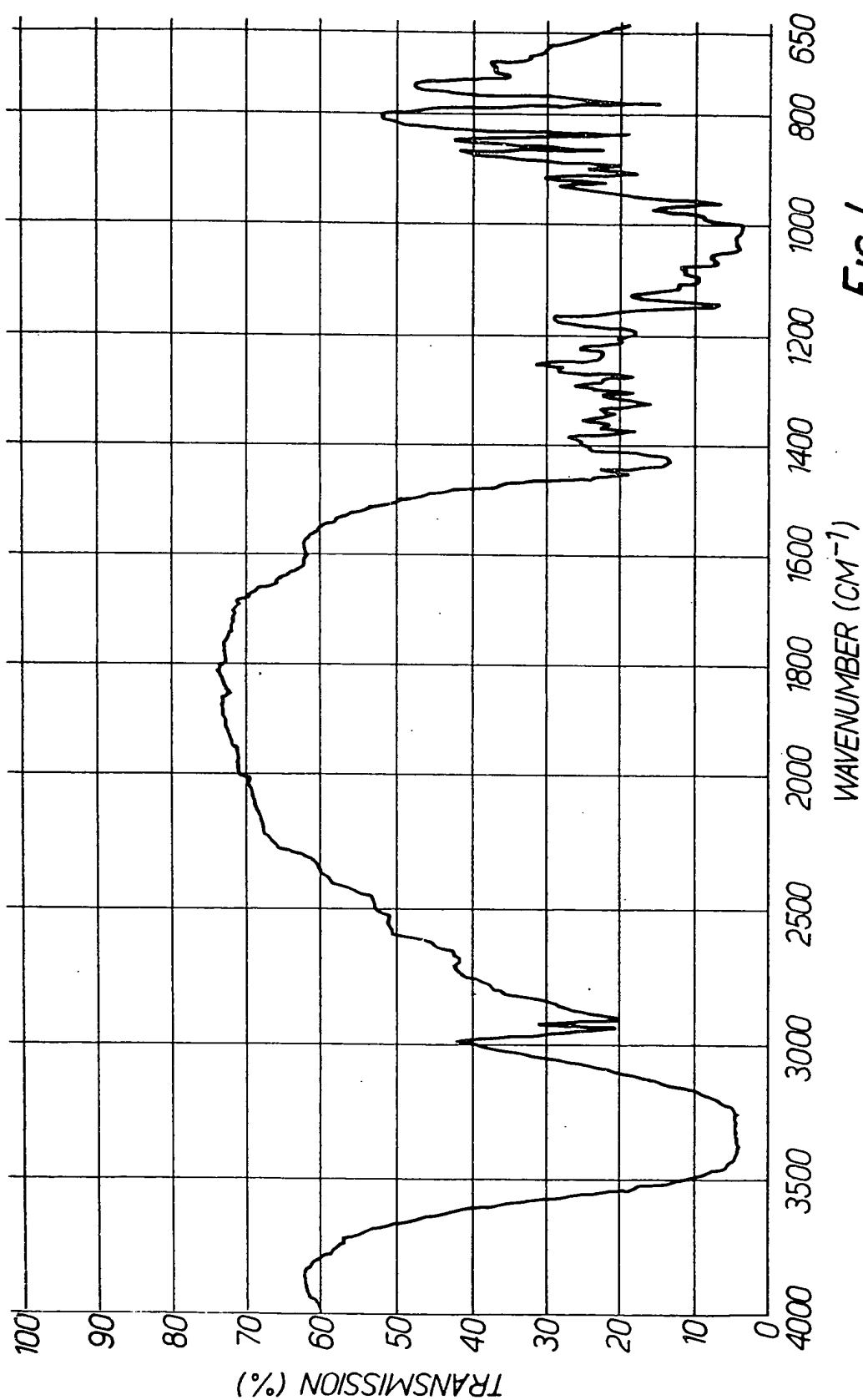


FIG. 1.

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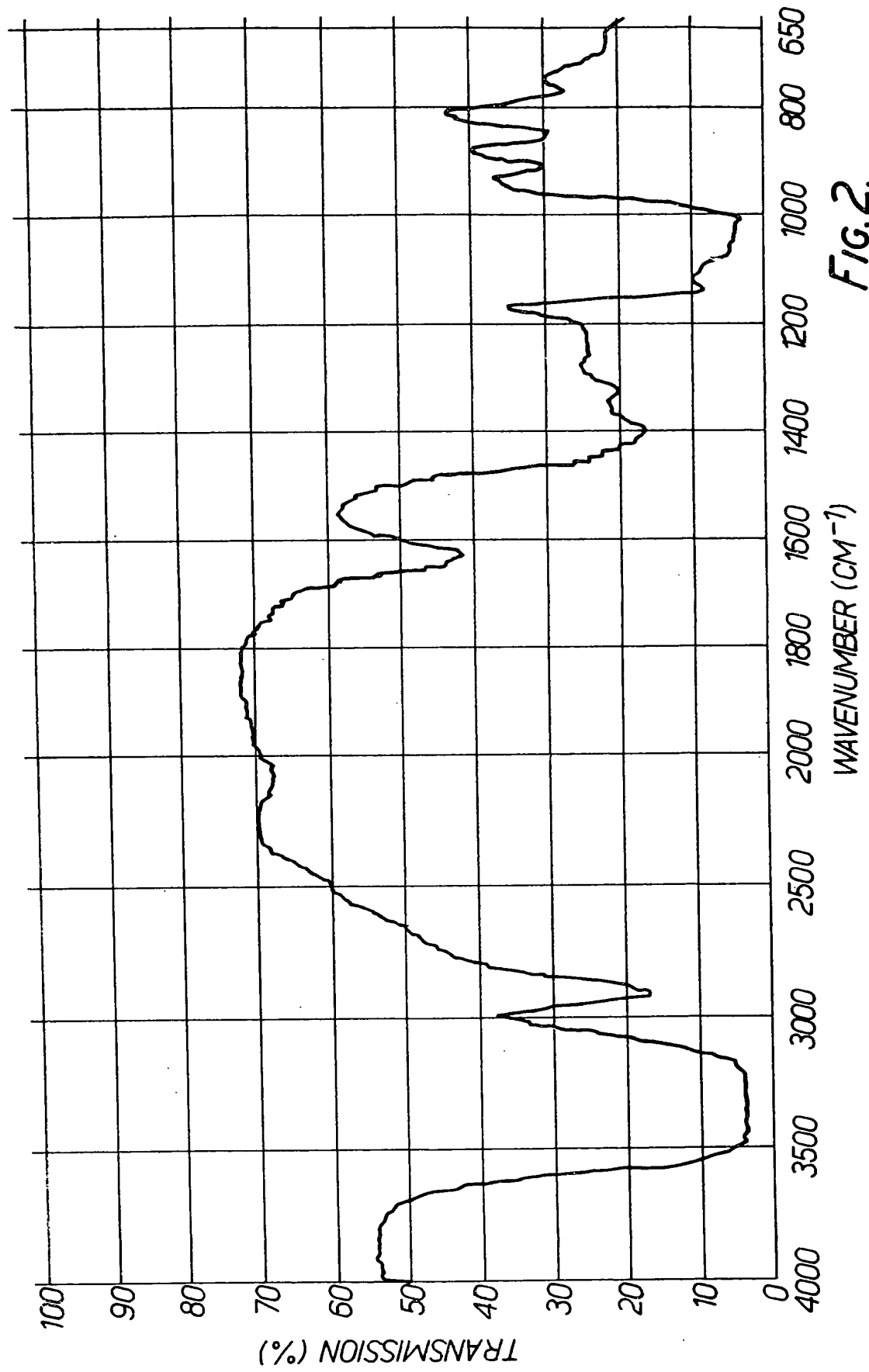


FIG. 2.

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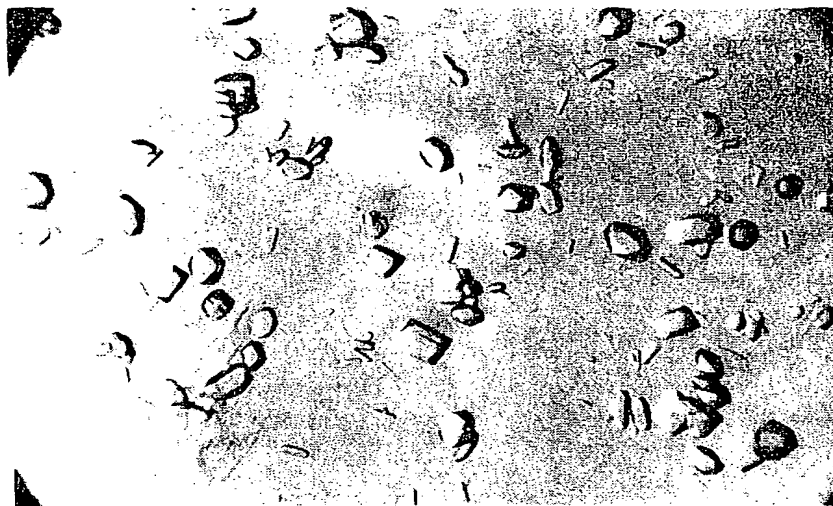


FIG. 3.

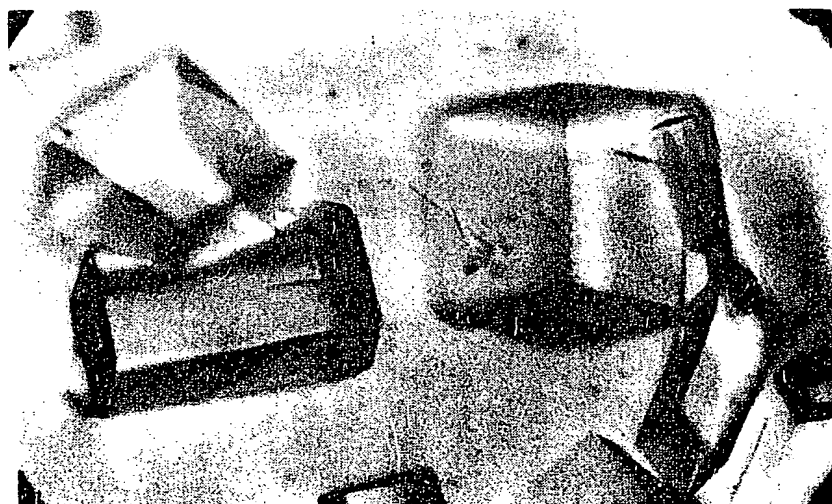


FIG. 4.

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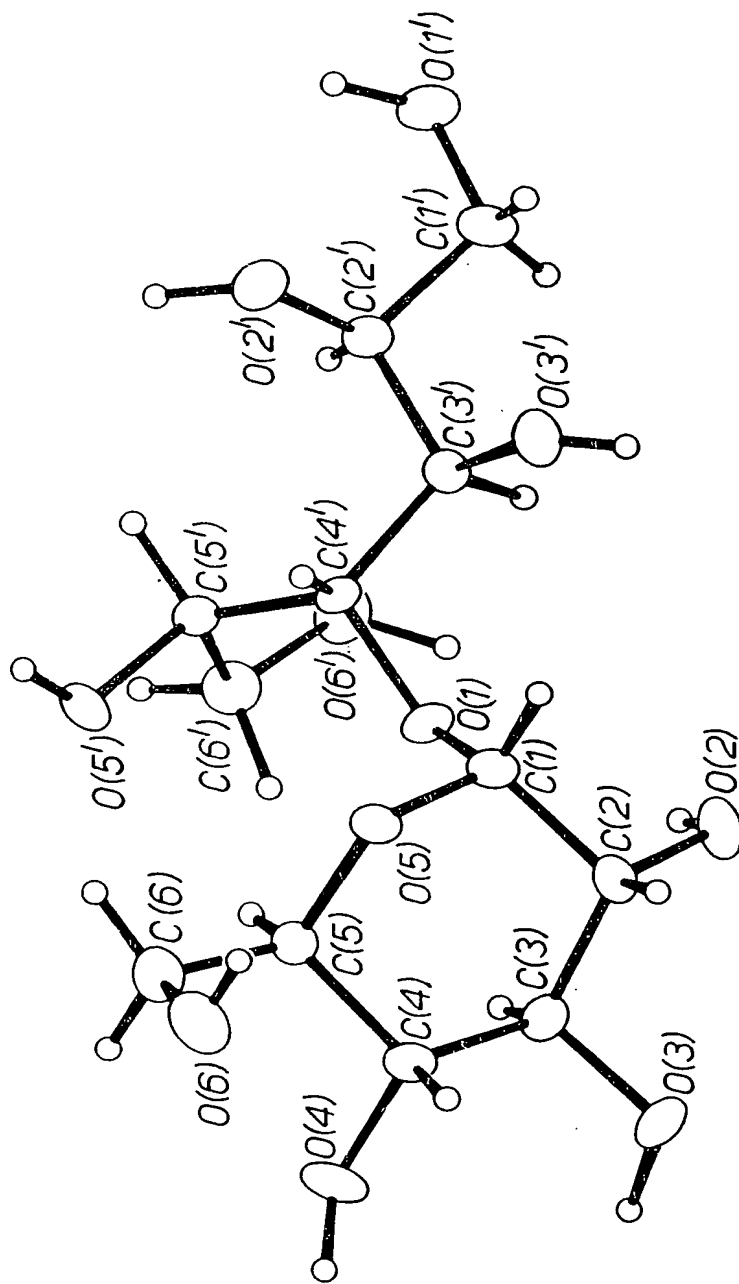


FIG. 5.

## SPECIFICATION

## Crystalline anhydrous maltitol

The present invention relates to crystalline anhydrous maltitol and a hydrogenated starch hydrolysate solid maltitol mixture containing said crystals, and to processes for the production thereof.

As described in Japanese Patent Publication No. 13,699/72 (MITSUHASHI *et al.*), maltitol is obtained by reduction of maltose. It has a sweetness which is close in quality to that of sucrose, and has a sweetening power about 75% higher than that of sucrose.

Since maltitol is practically not absorbed in the digestive system, and is barely fermentable by oral microorganisms, it has been used as a sweetener for low-caloric, dietary, low-cariogenic and health foods for diabetics, persons who are overweight and those who are conscious of their health including dental health.

However, since maltitol in dry solid form is extremely hygroscopic and deliquescent, and difficult to prepare into powder, it is usually handled only in the form of an aqueous solution. Its use has therefore been extremely restricted. For example, amorphous, substantially-anhydrous sweets can be obtained by boiling down an aqueous maltitol solution at 180—190°C, but the sweets must be stored in a moisture proof container together with a desiccant owing to their high hygroscopicity and deliquescence. Handling of the sweets is fraught with difficulty.

Previous reports of the hygroscopic properties of maltitol indicate that only a highly hygroscopic maltitol solid has been known hitherto. M. J. Wolfrom *et al.* have reported in J. Am. Chem. Soc., Vol. 62, pp. 2553—2555 (1940), that maltitol had been obtained only in the form of an amorphous, white, hygroscopic solid; and J. E. Hodge *et al.* reported in Cereal Science Today, Vol. 17, No. 7, pp. 180—188 (1972) that they had not yet obtained a non-hygroscopic solid form of maltitol and that maltitol could be crystallised as a hygroscopic ethanol complex.

There have recently been reports of many attempts to reduce as much as possible the high hygroscopicity of maltitol and also to obtain maltitol in powder form. For example, Japan Kokai No. 477/74 (UENO, Kunio *et al.*) and 87,619/74 (HIDAKA, Yoshio *et al.*) disclose processes for the production of maltitol powder by mixing a hydrophilic polymer, such as an edible polymer, to an aqueous maltitol solution, and drying the mixture to obtain the desired powder. Japan Kokai No. 59,312/75 (HISANO, Kazuaki *et al.*) discloses a process for the production of maltitol powder which comprises mixing a composition containing maltitol with a small amount of one or more mono-saccharides or their sugar alcohol derivatives, melting the mixture by heating to the anhydrous fused form, cooling the resultant material, and spray-drying and fluidising in a moisture proof tower to obtain the desired maltitol powder. Japan Kokai No. 110,620/74

(HIRAIWA, Takashi), 24,206/75 (HIRAIWA, Takashi *et al.*), 25,514/75 (OYAMADA, Ko-ichiro *et al.*), 32,745/76 (HIRAIWA, Takashi), 106,766/76 (HIRAIWA, Takashi), 113,813/76 (HIRAIWA, Takashi), 128,441/76 (HIRAIWA, Takashi) and 47,928/77 (HIRAIWA, Takashi) disclose processes for the production of maltitol powder which comprises pulverizing maltitol solid under dried air conditions, and coating on the resultant maltitol powder with other edible powder. Japan Kokai No. 29,510/75 (KANE-EDA, Jun *et al.*) discloses a method for preventing consolidation of a powder containing maltitol wherein a powder containing maltitol is moistened with a solvent which substantially indissolves maltitol, and dried together with other sugar micro-powder under mixing conditions to apply coating on the particles of maltitol powder with the micro-powder.

However none of these earlier attempts have proved successful because maltitol must be mixed with a large amount of other substance(s) or coated therewith, and the high hygroscopicity of maltitol cannot be eliminated thereby. In effect, the maltitol powder obtained by any of the above described processes barely retains its powder form under ambient conditions, and still exhibits its high hygroscopicity. Such powder is readily susceptible to moisture-absorption, consolidation and/or deliquescence under ambient conditions within a short time, and is unsuitable for practical uses.

According to a first aspect of the present invention there is provided anhydrous maltitol in crystalline form.

According to a second aspect of the present invention there is provided a crystalline hydrogenated starch hydrolysate solid mixture containing anhydrous maltitol in crystalline form.

In this specification the term "crystalline solid maltitol mixture" is used to mean crystalline hydrogenated starch hydrolysate solid mixture containing crystals of anhydrous maltitol, together with other sugar alcohols, such as sorbitol, maltotriitol and maltotetraitol.

We have found that crystals of anhydrous maltitol can be obtained as follows: A liquefied starch solution with a low Dextrose Equivalent value (abbreviated as "DE" hereinafter), is subjected to the enzymatic actions of isoamylase (EC 3.2.1.68) and  $\beta$ -amylase (EC 3.2.1.2) to obtain a saccharified starch solution with a high maltose content, and the saccharified starch solution is then subjected to purification, concentration, crystallisation and separation, obtaining a crystalline production with a maltose content of about 99% on dry solid basis (all "percentages" used hereinafter mean "percentages on dry solid basis" unless specified otherwise). Thereafter, an aqueous solution of the product is hydrogenated in the presence of Raney nickel catalyst, obtaining a maltitol solution with a high maltitol content up to about 98.5%. The maltitol solution is concentrated to 75%, and is allowed to stand for about six-months from 35 to

5°C in a soft-glass vessel to effect crystallisation. Then, the crystals grown on the vessel wall are added as seed crystals to an 80% aqueous maltitol solution with the high maltitol content, and the mixture is then subjected to crystallisation under gentle stirring conditions, obtaining a masquite which is then separated into mother liquor and maltitol crystals. The crystals are washed by spraying a small amount of water, and recrystallised similarly as above after dissolution in water, obtaining anhydrous maltitol crystals of high purity.

Physical and chemical investigations on the said crystals led to the finding that the crystals are anhydrous maltitol crystals which have been hitherto unknown.

The following physical and chemical properties of the crystals of anhydrous maltitol were determined:

(1) Elemental analysis: C, 41.9%; H, 7.1%; and O, 51.0% (Found); C, 41.86%, H, 7.03%; and O 51.11% (Calculated) for  $C_{12}H_{24}O_{11}$

(2) Molecular weight: 344.3

(3) Melting point: 146.5—147.0°C

(4) Specific rotation:  $[\alpha]_D^{20} +106.5^\circ$  (0.1 g per cc water)

(5) Ultraviolet absorption: no characteristic absorption is observed when dissolved in water

(6) Infrared absorption:

(a) Infrared spectrum of crystalline anhydrous maltitol: 5 mg crystals of anhydrous maltitol in powder form and 220 mg KBr were mixed, and pressed into a transparent tablet, about 0.6 mm thick, which was then subjected to infrared spectrometry. The resultant I.R. spectrum is shown in Figure 1 of the accompanying drawings.

(b) Infrared spectrum of amorphous, anhydrous maltitol: 3 mg crystals of anhydrous maltitol and 220 mg KBr were dissolved in hot water, and the mixture was dried, and pressed into a transparent tablet, about 0.8 mm thick, which was then subjected to infrared spectrometry.

The resultant I.R. spectrum is shown in Figure 2.

(7) Solubility: 100 g water dissolves up to 165 g crystals of anhydrous maltitol at 25°C

(8) Heat of dissolution: upon dissolution of 1 mole crystals of anhydrous maltitol in 190 mole water at 15°C, 5.5 Kcal is endothermically absorbed

(9) Appearance and properties: colourless, odourless, transparent crystals (micro-crystals in lump white). Figures 3 and 4 of the accompanying drawings show microphotographs of crystals of anhydrous maltitol grown from an aqueous maltitol solution. Figure 3 is magnified 150 times and Figure 4 is magnified 600 times. No hygroscopicity and deliquescence are observed. Weight reduction upon heating at 130°C for two hours is 0.5% or less. An aqueous solution of crystals of anhydrous maltitol is neutral or weakly acidic. It is sweet tasting.

(10) Solubility in various solvents: readily soluble in water, 0.1 N NaOH and 0.1 N HCl; soluble in methanol and ethanol; and insoluble in

chloroform and ethyl acetate

(11) Colour reaction; anthronesulfuric acid reaction, green; Fehling reduction reaction, negative; and  $I_2$  test, negative

(12) Sugar components:

(a) Acid hydrolysis using 1 N sulfuric acid, and subsequent paper and gas-liquid chromatographic analyses confirmed the presence of equimolar D-glucose and D-sorbitol fractions

(b) Complete methylation, hydrolysis and subsequent gas-liquid chromatographic analysis confirmed the presence of equimolar 2,3,4,6-tetra-O-methyl-D-glucose and 1,2,3,5,6-penta-O-methyl-D-sorbitol fractions

(c) The high specific rotation,  $[\alpha]_D^{20}$ , of  $+106.5^\circ$  and the infrared absorption neighbouring  $840\text{ cm}^{-1}$  suggest the presence of an  $\alpha$ -linkage between the glucose and sorbitol moieties

(d) Paper, gas-liquid and high-pressure liquid chromatographic analyses on the crystals of anhydrous maltitol gave the same single spot or peak at the same position as in the analyses on a commercial authentic maltitol preparation (special grade reagent)

(13) X-ray crystal structure: X-ray crystallographic study on a maltitol single crystal grown from a 75 w/w% supersaturated aqueous maltitol solution at 40°C gave the following crystal structure; orthorhombic, space group,  $P2_12_12_1$ ; lattice constants,  $a=8.166\text{ \AA}$ ,  $b=12.721\text{ \AA}$ ,  $c=13.629\text{ \AA}$ ; a stereo-scopic ORTEP figure is shown in Figure 5 of the accompanying drawings.

The above described physical and chemical properties of the maltitol crystals led to the conclusion that the present crystals are hitherto unknown crystals of anhydrous maltitol, and not a sugar hydrate, such as  $\beta$ -maltose mono-hydrate, nor the reported ethanol complex.

The following description illustrates the process for the production of crystals of anhydrous maltitol and of a "crystalline solid maltitol mixture" according to the invention.

As regards the maltitol solution which is subjected to crystallisation according to the invention, any maltitol solution can be used regardless of its method of production as long as crystals of anhydrous maltitol can grow from the solution by the addition of seed crystals at a supersaturated concentration. Usually, an aqueous maltitol solution, prepared with a sugar alcohol mixture having a maltitol content at least 65% to give a concentration, preferably of 65—95% (super-saturation degree of about 1.05—1.50), is subjected to crystallisation at a temperature in the range of 0—95°C, a range wherein the freezing of the solution does not occur, and wherein the heat loss is relatively low.

The supersaturation degree and viscosity of the solution can be regulated by the addition of water-soluble organic solvent, e.g., methanol, ethanol or acetone.

Crystallisation of the solution is usually started in a crystalliser at a relatively elevated temperature of about 40—95°C and a supersaturated concentration, and the solution is

cooled gradually with gentle stirring to obtain a mascuite containing crystals of anhydrous maltitol. In this case, the presence of seed crystals in an amount of 0.1—20.0% can accelerate the crystallisation.

As described above, crystals of anhydrous maltitol can be easily crystallised from a supersaturated aqueous maltitol solution by adding thereto a small amount of crystals of anhydrous maltitol or of the "crystalline solid maltitol mixture" as seed crystals.

The mascuite thus obtained can be separated into the crystals of anhydrous maltitol and mother liquor by a conventional separation method, or prepared into a "crystalline solid maltitol mixture" by conventional total-sugar method such as block-pulverisation, fluidised-bed granulation or spray-drying.

The separation method usually comprises transferring the mascuite into a basket-type centrifugator, separating the mascuite into crystals of anhydrous maltitol and mother liquor, and washing the crystals, if desired, by spraying them with a small amount of chilled water to obtain crystals of anhydrous maltitol of a higher purity.

The total-sugar method does not give maltitol of higher purity, but realises a higher yield of a "crystalline solid maltitol mixture". The crystalline solid mixture obtained by any of the three methods inevitably contains, besides crystals of anhydrous maltitol, other sugar alcohols—such as sorbitol, maltotriitol and maltotetraitol—derived from the constituents of the starting material starch syrup.

In spray-drying, a mascuite with a concentration of about 70—85%, in which crystallisation up to about 25—60% has occurred, is spray-dried through a nozzle equipped at the top of a spray-drying tower, by a high-pressure pump at a temperature at which the obtained crystalline powder does not melt, and which is maintained, for example, by introducing hot air at 60—100°C. Thereafter, the crystalline powder is aged by supplying air at 30—60°C for about one to twenty hours to give a non- or substantially-non-hygroscopic "crystalline solid maltitol mixture".

The block-pulverisation method usually comprises standing for  $\frac{1}{2}$  day to 5 days a mascuite with a moisture content of about 5—15%, wherein crystallisation up to about 10—60% has occurred, so as to solidify the mascuite into blocks which are then converted into powder by scraping, pulverising and subsequently drying.

A further total sugar method comprises adding seed crystals of anhydrous maltitol to a supersaturated melt prepared by concentrating an aqueous maltitol solution to a moisture content less than 5% by heating according to conventional method, the mixture then being kneaded at a temperature below its melting point to give a "crystalline maltitol solid mixture" which may be shaped into a desired shape, e.g. granules, rods, plates or cubes, or may be formed into powder.

Although dependent upon purity, the hygroscopicity of crystals of anhydrous maltitol or of the "crystalline solid maltitol mixture" slightly varies, these materials are substantially non-hygroscopic and free flowing. They are therefore suitable for various uses, e.g., for producing foods, drinks, cosmetics, drugs and chemical materials, or can be formed into desired shapes, in a manner similar to granulated sucrose, without fear of sticking and consolidation. Also, the physical properties of crystals of anhydrous maltitol and of the "crystalline solid maltitol mixture", such as melting point and specific rotation, vary according to their purities. As the purity decreases, the melting point falls and widens its range. For example, the melting point of a "crystalline solid maltitol mixture" with a maltitol content of 85.2% is 120—127°C. Accordingly, the purity of both products can be selected freely in accordance with the intended use thereof.

Additionally, since like sucrose crystals of anhydrous maltitol and the "crystalline solid maltitol mixture" dissolve readily in the mouth, and endothermically absorb more heat, they exhibit a pleasant refreshing taste; they are therefore desirable sweeteners.

Although crystals of anhydrous maltitol and the said "crystalline solid maltitol mixture" dissolve readily and quickly in water, they are substantially non-hygroscopic: thus, they are advantageously suitable for sweetening powder foods and drinks as described hereinafter.

Based on the above described features, the present invention enables industrial-scale production of maltitol containing foods and drinks, such as sweeteners in powder or solid form, fondant, chocolate, chewing gum, powdered juice or soup; and shaped bodies such as granules or tablets, which could not be prepared or were very difficult to prepare with conventional maltitol. Furthermore, since crystals of anhydrous maltitol and "crystalline solid maltitol mixture" are free flowing due to their non-hygroscopicity and low-susceptibility to consolidation, they lead to savings in the cost of labour, packing, transportation and storage.

Crystals of anhydrous maltitol and the "crystalline solid maltitol mixture" are readily soluble in water, satisfactorily heat- and acid-resistant, low-calorific, low-cariogenic and low-fermentable, and impart an appropriate sweetness, viscosity, body and gloss to foods and drinks, similarly as conventional maltitol; thus, their superior properties make the production of foods, drinks, drugs and cosmetics more feasible.

The maltitol crystals or the solid mixture of the invention can be used as a sweetener without further processing, or, if necessary, in combination with other conventional sweeteners, e.g., starch syrup solid, glucose, maltose, isomerised sugar, sucrose, honey, maple sugar, sorbitol, dihydrocharcone, stevioside,  $\alpha$ -glycosyl stevioside, sweet extract from *Momordica grosvenori*, glycyrrhizin, L-asparatyl phenyl-

alanine methyl ester, saccharin, glycine and/or alanine; and/or in combination with fillers, e.g., dextrin, starch and/or lactose.

Also, they can be used intact, or mixed, if necessary, with fillers, vehicles and/or binders, and then formed into a desirable shape, e.g., granules, spheres, tablets, rods, plates or cubes.

Like conventional maltitol, the maltitol materials of the present invention are hardly absorbed and used by the digestive system, and a reduction in the calorific value of foods and drinks can be realised therewith without changing their desirable properties: thus, they are favourably usable as a low-calorific sweetener, and for sweetening low-calorific foods and drinks, e.g., dietary and health foods, for diabetics, obese persons and those whose calory-intakes are restricted.

Furthermore, since both products are hardly fermentable by dental caries-causative microorganisms, similar to conventional maltitol, they can also be favourably used as a low-cariogenic sweetener for confectionery e.g., chewing gum, chocolate, biscuits, cookies, caramel, and candy; and in soft drinks, e.g., cola drinks, cider, juice, coffee and yoghurt. Also, they are favourably useable for reducing the cariogenicity of cosmetics and drugs, such as mouth washes and tooth paste, by replacing sucrose therein, as well as for sweetening them.

The sweetness of the maltitol products of the present invention harmonises well with sour, salty, astringent, sweet and/or bitter tasting substance(s) as well as being highly acid- and heat-resistant. Thus, in addition to the above described special uses, they are also suitable for sweetening foods and drinks in general, and improving their taste qualities. For example, they may be used in seasonings such as sauce, soy sauce, soy sauce powder, soy sauce paste "MISO", soy sauce paste powder, mayonnaise, dressing, vinegar, vinegar powder, extracts for Chinese-style foods, catsup, curry roux, extracts for stew and soup, mixed seasonings and table and coffee sugars; confectionery and bakery products such as Japanese-style confectionery, jelly, castella, bread, biscuits, crackers, cookies, pies, puddings, butter cream, custard cream, choux cream, cream puffs, waffles, sponge cakes, doughnuts, chocolate, chewing gum, caramel and candy; frozen desserts such as icecream and sherbet; syrups; pastes such as peanut paste, flour paste and fruit paste; pickles and preserves such as jam, marmalade, preserves, processed vegetables and pickles; pickle additives; meat products such as ham and sausage; processed fish products such as ham and sausage; preserved foods; products such as cooked beans and potato salad; canned and bottled foods such as those of fish, meat, fruit, vegetable and shellfish; alcoholic drinks such as wine, whisky and brandy; soft drinks, such as coffee, cocoa, juice, carbonated drinks, lactic acid drinks and yoghurt drinks; and convenience foods and drinks such as puddings, cakes, juices, coffee and soup.

The maltitol products of the invention are non-hygroscopic and free flowing. They are therefore suitable for improving the properties of pre-packed foods, and/or preventing the sticking and adhesion of the content on the package, for example, as in the case of chewing gum.

Additionally, they are suitable for improving the tastes of pet foods or feeds for domestic animals or fowl; honey bee, silkworm or fish, as well as for sweetening and improving the tastes of tobacco, cosmetics and drugs which are in the form of solid, liquid or paste, such as tooth paste, lipstick, lipcream, drugs for internal administration, troche, cod-liver oil drops, cachou, gargles and oral refreshing agents.

The maltitol products according to the invention can be prepared into any desirable shape by spraying a small amount of water or an aqueous maltitol solution thereon to slightly moisten them, and molding the resultant material under a slightly elevated pressure, as in the case of sucrose; for example, in the shape of a fish, animal, cube or flower. Thus, a shaped sweetener for coffee or tea in any desirable shape can be easily prepared. To the shaped sweetener can be added other sweeteners, e.g.,  $\alpha$ -glycosyl stevioside, sucrose and/or saccharin to further enhance the sweetness; colouring agent, for example, red or green; and/or flavour such as orange-, coffee or brandy flavour. In flavouring, the objectives may be attainable with the use of a flavour-cyclodextrin complex (a host-guest complex).

Furthermore, like sucrose the present maltitol products can be easily obtained in massive form, and they are therefore suitable for use as semi- or transparent sweetener solid in place of the conventional candy sugar or coffee sugar.

Additionally, other substance(s), such as for example vitamins, antibiotics or microorganisms of genus *Lactobacillus* can be added to the maltitol products of the present invention prior to shaping, and the mixture is then prepared into desirable shape. For example, granules are formed with a granuliser, or tablets are formed with a tableting machine.

As regards the methods for incorporating the maltitol products of the present invention into the above described foods, drinks, tobacco, pet foods, feeds, cosmetics, drugs or shaped bodies, any method can be employed in the invention as long as the said maltitol products are incorporated therein before the completion of processing. Preferable conventional methods are mixing, kneading, dissolving, dipping, melting, immersing, permeating, injecting, crystallising and solidifying.

In addition to the above described uses, maltitol products of the present invention are of low-moisture content of substantially anhydrous, and the small amount of moisture present therein can be removed completely by brief drying with hot air. They can therefore be favourably used in chemical reactions under anhydrous conditions. For example, etherification or esterification reaction of the said maltitol products under

anhydrous conditions leads to a higher yield of ether or ester derivatives of maltitol. The derivatives thus obtained can be favourably used, for example, as emulsifiers or surface-active agents.

The present invention is illustrated by the following Examples.

#### Example 1 Seed crystals

To a starch suspension, consisting of one part of potato starch and ten parts of water, was added a commercial liquefying  $\alpha$ -amylase, and the mixture was heated to 90°C to effect gelatinisation. The enzymatic liquefaction was suspended by immediately heating to 130°C, obtaining a liquefied starch solution with DE of about 0.5.

After cooling immediately the solution to 55°C, to the solution was added *Pseudomonas amyloclavata* (ATCC 21262) isoamylase (EC 3.2.1.68) in an amount of 100 units per g starch, and a soy bean  $\beta$ -amylase "Nagase & Company, Ltd., Osaka, Japan) in an amount of 50 units per g starch, and the mixture was saccharified at this temperature and pH 5.0 for 40 hours. Obtaining a saccharified starch solution with a high maltose content: glucose, 0.4%; maltose, 92.5% maltotriose, 5.0%; and higher oligosaccharides including maltotetraose, 2.1%.

The saccharified starch solution was purified by decolourisation with activated carbon, and deionisation with ion exchangers.

After concentrating the purified saccharified starch solution to 75%, the concentrate was transferred into a crystalliser, and  $\beta$ -maltose mono-hydrate was added thereto as seed crystals in an amount of 1%. The resultant admixture was then cooled gradually from 40°C to 30°C over a period of two days, followed by separation of the resultant masquite with a basket-type centrifugator into crystalline maltose and mother liquor. The crystalline maltose was washed by spraying with a small amount of water, obtaining a highly-purified maltose with a purity of 99.0%.

A 50% aqueous solution of the highly-purified maltose was placed in an autoclave, and added with Raney nickel catalyst in an amount of 10%. Thereafter, the content was heated to 90—125°C, and hydrogenation was effected at that temperature and a hydrogen pressure of 20—100 kg/cm<sup>2</sup>. After completion of the hydrogenation, the Raney nickel catalyst was removed, and the residual aqueous solution was purified by decolourisation with activated carbon, and deionisation with ion exchangers according to conventional method, obtaining a highly-purified maltitol solution with a purity of 98.5%.

After concentrating the highly-purified maltitol solution to 75% under a reduced pressure, a small portion of the concentrate was placed in a soft-glass vessel, and allowed to stand at 30—5°C for about six months to effect crystallisation, resulting in the growth of crystals of anhydrous maltitol on the vessel wall.

These crystals of anhydrous maltitol were added as seed crystals to an 80% aqueous maltitol solution, and the mixture was crystallised under gentle stirring conditions. The resultant masquite was then transferred into a basket-type centrifugator, and separated therein into crystals and mother liquor. The crystals were then washed by spraying with a small amount of water, obtaining a highly-purified crystal of anhydrous maltitol with a purity of 99.8%.

The crystals of anhydrous maltitol have the following physical properties: melting point, 146.5—147.0°C; 100 g water dissolves up to 165 g crystals of anhydrous maltitol at 25°C; and no hygroscopicity is observed under ambient conditions.

The crystals of anhydrous maltitol can be advantageously used as seed crystals in the production of further anhydrous crystals of maltitol or of the said crystalline solid maltitol mixture.

#### Example 2 Crystals of anhydrous maltitol

To a starch suspension, consisting of one part of potato starch and ten parts of water, was added a commercial *Bacillus* liquefying  $\alpha$ -amylase, and the mixture was then heated to 90°C to effect gelatinisation. The enzymatic liquefaction was suspended immediately by heating the mixture to 130°C, obtaining a liquefied starch solution with a DE of about 0.5. The solution was then immediately cooled to 50°C, and added with an *Escherichia intermedia* (ATCC 21073) pullulanase (EC 3.2.1.41) in an amount of 50 units per g starch, and a soy bean  $\beta$ -amylase "Nagase & Company, Ltd., Osaka, Japan) in an amount of 30 units per g starch. The enzymatic saccharification was continued at this temperature and pH 6.0 for 46 hours, and the saccharified starch solution was decolourised with activated carbon, and subsequently deionised with ion exchangers, obtaining a maltose solution with a sugar composition of glucose, 0.4%, maltose, 92.5%, maltotriose, 4.8%, and higher oligosaccharides including maltotetraose, 2.3%, in a yield of about 97% against the starting starch material.

After adjusting the concentration of the maltose solution to 50%, to the concentrate was added Raney nickel catalyst in an amount of 10%, and the admixture was then heated to 90—125°C under the stirring conditions, and hydrogenated at this temperature under a hydrogen pressure of 20—100 kg/cm<sup>2</sup>. After completion of the hydrogenation, the Raney nickel catalyst was removed, and the hydrogenated product was purified with activated carbon and ion exchangers according to conventional method, obtaining a sugar alcohol mixture with a composition of sorbitol, 0.8%, maltitol, 92.2%, maltotriitol, 4.6%, and higher sugar alcohols including maltotetraitol, 2.4%, in a yield of about 92% against the starting starch material.

After concentrating the mixture to 80%, the

concentrate was then transferred into a crystalliser, crystals of anhydrous maltitol in powder form were added as seed crystals in an amount of 1%, and the concentrate was cooled gradually from 50°C to 20°C over a period of three days under stirring conditions. The resultant mascuite was separated with a basket-type centrifugator into crystals and mother liquor. The crystals were washed by spraying with a small amount of water, obtaining the crystals of anhydrous maltitol with a maltitol content of 99.2% in the yield of about 46% against the starting starch material.

The melting point of the product was 146.5—147.0°C.

The product is highly pure and non-hygroscopic: thus, it is suitable for use as a chemical material and as a sweetener and/or taste-improving agent for various foods, drinks, cosmetics and drugs.

### Example 3

#### Crystalline solid maltitol mixture

To a starch suspension, consisting of three parts of corn starch and ten parts of water, was added a commercial *Bacillus* liquefying  $\alpha$ -amylase, and the mixture was heated to 90°C to effect gelatinisation. The enzymatic liquefaction was suspended by heating immediately the mixture to 130°C, obtaining a liquefied starch solution with a DE of about 3.

After cooling immediately the solution to 55°C, to the solution was added *Pseudomonas amyloclavata* (ATCC 21262) isoamylase (EC 3.2.1.68) in an amount of 100 units per g starch, and a soy bean  $\beta$ -amylase "N1500" (Nagase & Company, Ltd, Osaka, Japan) in an amount of 30 units per g starch, and the mixture was kept at this temperature and pH 5.0 for 36 hours to effect enzymatic saccharification. The saccharified starch solution was purified similarly as in Example 2, obtaining a maltose solution with a sugar composition of glucose, 2.6%, maltose, 85.4%, maltotriose, 7.4%, and higher oligosaccharides including maltotetraose, 4.6%.

Then, the hydrogenation of the maltose solution was carried out similarly as in Example 2, obtaining a sugar alcohol mixture with a composition of sorbitol, 3.6%, maltitol, 85.4%, maltotriitol, 6.8%, and higher sugar alcohols including maltotetraitol, 4.6%.

Thereafter, the mixture was concentrated to 88%, and the concentrate was transferred into a crystalliser, crystals of anhydrous maltitol in powder form were added as seed crystals in an amount of 2%, and kept at 50°C for two hours under gentle stirring conditions. The mixture was then placed in plastic vessels where it was allowed to stand at 20°C for 4 days to effect solidification. The obtained blocks were removed from the vessels, and pulverised by a crusher equipped with a scraper. The powder was dried to obtain a "crystalline solid maltitol mixture" in a yield of 90% against the starting starch material.

The melting point of the product is 120—127°C.

The product is substantially nonhygroscopic and readily handleable; thus, it is suitable for improving the tastes of various foods, drinks, cosmetics and drugs as well as for sweetening them.

### Example 4

#### Crystalline solid maltitol mixture

After concentrating a sugar alcohol mixture, obtained similarly as in Example 2, to 80%, the concentrate was then transferred into a crystalliser, and 2% of "crystalline solid maltitol mixture" in powder form was added as seed crystals. The mixture was cooled gradually from 50°C with gentle stirring, obtaining a mascuite wherein the crystallisation had proceeded up to 35%. The mascuite was then spray-dried via a 1.5 mm $\phi$  nozzle, equipped at the top of a spraying tower, with a high-pressure pump at a pressure of 150 kg/cm<sup>2</sup>. Simultaneously, hot air at 85°C was passed downwards from the top of the tower to collect the pulverised product on a net conveyor placed at the bottom of the tower, and to fluidise the product out of the tower over a period of 40 minutes while passing a stream of air at 40°C upwards through the net. The resultant product was then transferred into an ageing tower, and aged therein for ten hours to effect complete crystallisation and drying, obtaining a "crystalline solid maltitol mixture" in a yield of about 92% against the starting starch material.

The product is nonhygroscopic and readily handleable; thus, it is advantageously usable in various chemical materials as well as in sweeteners.

### Example 5

#### Fondant

A starch suspension, consisting of five parts of corn starch and ten parts of water, was liquefied similarly as in Example 3, obtaining a liquefied starch solution with DE of 5.

After cooling immediately the solution to 55°C, to the solution was added the isoamylase in an amount of 70 units per g starch and  $\beta$ -amylase in an amount of 10 units per g starch, and the mixture was kept at this temperature and pH 5.0 for 36 hours to effect enzymatic saccharification. The mixture was then purified similarly as in Example 2 to obtain a saccharified starch solution with a sugar composition of glucose, 0.9%, maltose, 77.6%, maltotriose, 12.5%, and higher oligosaccharides including maltotetraose, 9.0%.

The solution was then hydrogenated similarly as in Example 2, obtaining a sugar alcohol mixture with a composition of sorbitol, 1.4%, maltitol, 77.3%, maltotriitol, 12.3%, and higher sugar alcohols including maltotetraitol, 9.0%.

After concentration of the mixture to 85%, the concentrate was transferred into a crystalliser, added with seed crystals in an amount of 1%, and then cooled to ambient temperature under

vigorous stirring conditions to effect crystallisation. Crystals of anhydrous maltitol obtained similarly as in Example 2 were added to the resultant product to obtain the fondant product.

The product is a white paste with a smooth and mild sweetness: thus, it is suitable for use as a material for confectionery.

#### Example 6

##### 10 Sweetener

A mixed sweetener was prepared by mixing homogeneously one part of "crystalline solid maltitol mixture" in powder form, obtained similarly as in Example 3, and 0.05 parts of a commercial  $\alpha$ -glycosyl stevioside " $\alpha$ -G-Sweet" (Toyo Sugar Refining Co., Ltd., Tokyo, Japan).

The mixed sweetener has an excellent sweetness which is about two-fold higher in sweetening power than that of sucrose, but having a calorific value about one-twentieth of that of sucrose. The sweetener is thus suitable for use in various low-calorific foods and drinks for diabetics, obese persons and those whose calorie-intakes are restricted. Additionally, since neither acid- nor water insoluble glucan formation by dental caries causative-microorganisms is observed, it is advantageously usable for sweetening various low-cariogenic foods and drinks.

##### 30 Example 7 Cube maltitol

One part of crystals of anhydrous maltitol obtained as in Example 2, and 0.01 part of saccharin were mixed until a homogeneous mixture was obtained. After moistening the mixture by spraying a small amount of an aqueous maltitol solution onto it, it was formed into cubes using molds for conventional cubic sugar under a relatively elevated pressure, and the cubes were removed from the molds, to give cubes of anhydrous maltitol.

The product is a white, nonhygroscopic cubic material with sufficient physical strength and about two-fold higher sweetening power in comparison with that of sucrose as well as being readily soluble in cold water. It is an ideal low-calorific and low-cariogenic sweetener.

##### Example 8 Cream wafers

A creamy product, prepared by mechanical mixing of a mixture consisting of 2,000 parts of a "crystalline solid maltitol mixture" in powder form obtained as in Example 3, 1,000 parts of shortening, one part of lecithin, one part of lemon oil and one part of vanilla oil, according to conventional method, was kept at 40—45°C, and sandwiched between wafers to obtain cream wafers.

##### 60 Example 9 Custard cream

Five hundred parts of corn starch, 500 parts of a "crystalline solid maltitol mixture" in powder

form obtained as in Example 4, 400 parts of maltose and 5 parts of NaCl were mixed by shifting and sieving, and the mixture was added with 1,400 parts of egg, followed by stirring. Then, the mixture was gradually added with 5,000 parts of boiling milk while stirring and heating at low heat. The heating was stopped when the corn starch gelatinised and the mixture became transparent. Then, to the cooled mixture was further added a small amount of vanilla flavour to obtain a custard cream product.

The product is a smooth, glossy and very delicious custard cream with no excessive sweetness.

##### Example 10 Chocolate

A mixture, consisting of 40 parts of cacao base, 10 parts of cacao butter and 50 parts of crystals of anhydrous maltitol obtained as in Example 2, was placed in a refiner to reduce its viscosity. Then, the mixture was transferred into a conche, and kneaded sufficiently therein at 50°C for two days.

During the kneading step, 0.5 parts of lecithin was added thereto and dispersed.

Thereafter, the mixture was filled at 30°C under thermally-regulated conditions into molds just before its solidification. The mixture was degassed by vibration, and solidified by passing through a 10°C cooling tunnel for 20 minutes. The contents of the molds were then removed, and packed to give a chocolate product.

The product is a non-hygroscopic chocolate with a mild and elegant flavour, excellent colour and satisfactory brightness and texture, and melts smoothly in the mouth. It is an ideal low-cariogenic and low-calorific chocolate.

##### 100 Example 11 Chocolate coated candy

A mixture, consisting of 95 parts of a "crystalline solid maltitol mixture" in powder form obtained as in Example 3, 5 parts of corn syrup and a small amount of water, was homogenised by stirring to fluid state. Then, to the mixture was added small amounts of flavour and colouring agent, and the mixture was poured with a depositor in molds in layered starch, and solidified partially therein. The flour starch attached thereon was removed by shifting and sieving to obtain the centres for the chocolate coated candy. The centres were coated with an unsolidified chocolate, obtained similarly as in Example 10, cooled, solidified, and finally packed to obtain the chocolate coated candy.

##### Example 12 Chewing gum

Twenty-five parts of gum based and 40 parts of a fondant, obtained as in Example 5, were kneaded at 60°C by a mechanical mixer. To the mixture was added 30 parts of crystals of anhydrous maltitol obtained as in Example 2, 1.5 parts of calcium phosphate, 0.1 part of L-menthol- $\beta$ -

cyclodextrin complex (a host-guest complex), and small amounts of condiments, and the mixture was then kneaded, rolled and cut according to conventional methods to obtain a chewing gum product.

The product is an ideal low-cariogenic chewing gum.

### Example 13 Juice powder

Thirty-eight parts of juice powder obtained by spray-drying, was added with 60 parts of "crystalline solid maltitol mixture" in powder form obtained as in Example 4, 0.65 parts of citric anhydride, 0.1 part of malic acid, 0.1 part of ascorbic acid, 0.1 part of sodium citrate, 0.6 parts of a flavour powder and 0.5 parts of pullulan, and the mixture was kneaded.

Then, the mixture was granulated in a fluidised-bed granuliser wherein the mixture was first moistened by spraying thereon a 50% aqueous maltitol solution, obtained as in Example 3, at a rate of 100 ml per minute, and then fluidised into a powder over a period of 30 minutes by charging air at 40°C at a rate of 150 m<sup>3</sup> per minute.

The product thus obtained is a powdered juice with a powder orange juice content of about 30%, and is free from unpleasant odour and taste as well as being stable over long periods of storage without consolidation.

### Example 14 Convenience soup powder

A mixture, consisting of 30 parts of gelatinised corn powder, 5 parts of gelatinised wheat flour, 4 parts of gelatinised potato starch, 12 parts of gelatinised waxy corn starch, 8 parts of a "crystalline solid maltitol mixture" in powder form obtained as in Example 3, 5 parts of sodium glutamate, 8.5 parts of NaCl, 7 parts of defatted milk and 0.5 parts of onion powder, was crushed and mixed sufficiently. The mixture was then further added with 0.5 parts of a melted sorbitan aliphatic acid ester, 9 parts of a melted hydrogenated vegetable oil and 10 parts of lactose, and the mixture was mixed further.

The mixture was granulated as described in Example 13 in a fluidised-bed granuliser wherein the mixture was sprayed with a small amount of water, fluidised, and dried with hot air at 70°C.

Thereafter, the product was shifted and sieved to obtain a soup powder.

An addition of hot water to the product readily dissolves and disperses the product to give instantly a soup with an excellent flavour.

### Example 15 Extract of "UIRO"

A mixture, consisting of 90 parts of rice flour, 20 parts of corn starch, 120 parts of a "crystalline solid maltitol mixture" in powder form obtained as in Example 4, and 4 parts of pullulan, was kneaded to homogeneity to obtain Extract of "UIRO"—a type of Japanese-style rice paste confectionery.

Two hundred g of the extract and 1 g green tea powder ("MACCHA") were added with water, and the mixture was kneaded sufficiently. Then, the resultant mixture was placed in a vessel, and steamed therein for 60 minutes to obtain a "MACCHA UIRO".

The product is excellent in gloss, flavour and biting properties. Also, the retrogradation of the amylaceous components is sufficiently suppressed, and therefore the product is stable over the long period of storage.

### Example 16 Pickle additive for "BETTARA-ZUKE"

Four parts of a "crystalline solid maltitol mixture" in powder form obtained as in Example 3, 0.05 parts of sweet extract from *Licorice*, 0.008 parts of malic acid, 0.07 parts of sodium glutamate, 0.03 parts of potassium sorbate and 0.2 parts of pullulan were mixed and kneaded to homogeneity to give a pickle additive for "BETTARA-ZUKE"—a type of Japanese-style pickle.

Using conventional methods, 30 kg of Japanese radish ("DAIKON", *Raphanus sativus*) was partially pickled with NaCl, and then further pickled with sucrose. The final pickling was carried out in a seasoning solution, prepared with 4 kg of the said pickle additive, to obtain "BETTARA-ZUKE".

The product is moderately sweet, and excellent in colour, brightness, flavour and biting properties. Also, the product is stable over the long period of storage due to its low susceptibility to excessive fermentation.

### Example 17 Tablet

Fifty parts of acetylsalicylic acid, 14 parts of a "crystalline solid maltitol mixture" in powder form obtained as in Example 3, and 4 parts of corn starch powder were mixed and kneaded. Then, the mixture was tableted into tablets 5.25mm thick weighing 680 mg, using a conventional tableting machine.

The product is very moisture-resistant, and its physical strength is extremely high as well as being readily soluble in water.

### Example 18 Polyether derivative of maltitol

Three parts of crystals of anhydrous maltitol obtained as in Example 2, and 0.2 parts of pyridine were placed together in a reaction vessel. The mixture was added with 3 parts of dimethyl sulfoxide, and propylene oxide gas was then charged therein, while keeping the reaction temperature at 90—100°C. The reaction was suspended when about five parts of propylene oxide was consumed.

The solvents and residual reagent were removed by distillation at 120°C and a reduced pressure of about 10—20 mmHg under nitrogen atmosphere. The residue was cooled to about 60°C, added gradually with about 5 parts of conc.

hydrochloric acid with stirring, and further added with 5 parts of benzene to form salts which were then removed by filtration *in vacuo*. All benzene, water and hydrochloric acid were removed from the filtrate by distillation to obtain an about 8 parts of viscous oily polyether derivative of maltitol.

The derivative exhibits an excellent surface-active action. It is suitable for various uses, such as an emulsifier, thickener or moisture-retaining agent, as well as a surface-active agent for general use.

In addition to the above described uses, it can be used as a material in polyurethane production using isocyanate compounds.

#### Example 19

##### Fatty acid ester derivative of maltitol

Two parts of a "crystalline solid maltitol mixture" in powder form obtained as in Example 3, was dissolved in 7 parts of dimethyl formamide. To the solution was added 0.6 parts of methyl palmitate and 0.04 parts of potassium carbonate, and the mixture was subjected to ester-exchange reaction overnight at a pressure of about 100—200 mmHg and a temperature of about 80—100°C with stirring.

After completion of the reaction, the solvent was removed by distillation *in vacuo*, and the residue was washed twice with three parts of acetone. After concentration of the residue, the concentrate was washed with benzene and petroleum ether. The viscous oily product was immersed in three parts of acetone while heating, and the extract was allowed to stand under ice-cold conditions to yield a precipitate which was then treated with acetone, and dried to obtain 0.6 parts of maltitol mono-palmitate.

The derivative exhibits a satisfactory surface-active action. It is suitable for use as an emulsifier for foods as well as an ingredient for detergents.

#### Claims

1. Anhydrous maltitol in crystalline form.
2. Anhydrous maltitol according to Claim 1, and having a melting point of 146.5 to 147.0°C.
3. Anhydrous maltitol in crystalline form substantially as hereinbefore described in Example 1 or 2.
4. A crystalline hydrogenated starch hydrolysate solid mixture containing anhydrous maltitol in crystalline form.
5. A solid mixture according to Claim 4, having a maltitol content which is at least 65% on dry solid basis.
6. A solid maltitol mixture according to Claim 4, substantially as hereinbefore described in Example 3 or 4.
7. A process for the production of anhydrous maltitol in crystalline form or a solid maltitol

mixture according to Claim 4, which process comprises

(a) crystallising a solution containing maltitol and harvesting the resultant crystals of anhydrous maltitol from the solution, or

(b) crystallising a solution containing maltitol, and solidifying the resultant mascuite into a crystalline solid.

8. A process according to Claim 7, wherein the maltitol content of the solution is at least 65% on dry solid basis.

9. A process according to Claim 7 or 8, wherein the crystallisation is carried out at a temperature in the range of 0—95°C.

10. A process according to Claim 7 substantially as described in any one of the foregoing Examples 1 to 4.

11. A process for the production of food or drink, which process comprises including in the food or drink anhydrous maltitol as claimed in Claim 1, 2, or 3 or a solid maltitol mixture as claimed in Claim 4, 5 or 6.

12. A process according to Claim 11, wherein said food or drink is a sweetener.

13. A process according to Claim 11 or 12, wherein said food or drink is in powder form.

14. A process according to Claim 11 or 12, wherein said food or drink is in solid form.

15. A process according to Claim 11, wherein said food or drink is a sweetened, low-calorific food or drink.

16. A process according to Claim 11, wherein said food or drink is a sweetened, low-cariogenic food or drink.

17. A process according to Claim 11 substantially as hereinbefore described in any one of Examples 5 to 16.

18. A food or drink whenever prepared by a process as claimed in any one of Claims 11 to 17.

19. A process for the production of a shaped body, comprising forming into a desired shape a composition including crystals of anhydrous maltitol as claimed in Claim 1, 2 or 3 or a solid maltitol mixture as claimed in Claim 4, 5 or 6.

20. A process according to Claim 19, wherein said shaped body is formed from a powder.

21. A process according to Claim 19, wherein said shaped body is formed from granules.

22. A process according to Claim 21, wherein said shaped body is shaped into tablets.

23. A process for the production of a derivative of anhydrous maltitol which comprises subjecting crystals of anhydrous maltitol as claimed in Claim 1, 2 or 3, or a solid maltitol mixture as claimed in Claim 4, 5 or 6 to a chemical reaction under anhydrous conditions.

24. A process according to Claim 23, wherein the maltitol derivative is an ether or ester.

25. A process according to Claim 23 substantially as hereinbefore described in Example 18 or 19.